Superelastic Properties at Cryogenic Temperatures in Ti-Ni, Ni-Co-Mn-In and Cu-Al-Mn Shape Memory Alloys

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論 文 内 容 要 旨

Chapter 1: Introduction

Shape memory alloy (SMA) is a functional material that exhibits crystallographic change by applications of temperature change, stress and magnetic field. Being totally different from common metals, SMA undergoes such change without atomic diffusion, termed martensitic transformation (MT), during which the shape memory effect (SME) and the superelastic effect (SE) can be educed. By virtue of their exclusive functionalities, SME and SE have yielded huge opportunities for the design of applications. However, almost all the applications of SME and SE are limited to Ti-Ni-based alloys exhibiting the R-phase transformation and to the narrow temperature window around the ambient environment. With respect to the study on low-temperature applications, there have been fewer reports, especially below 77 K, in spite of their application potentialities in, for example, superconductive systems, next-generation fuels of liquefied gases, aerospace materials and cryogenic sealing materials. In addition, some anomalies in a cryogenic environment, such as the thermal transformation arrest (TTA) phenomenon in Ni-Mn-based metamagnetic SMA and the strain glass phenomenon in Ti-Ni-based SMAs, have been reported, attracting increasing interest from many researchers.

In this thesis, with an eye towards the low-temperature application of SMA and to clarify the fundamental curiosities about some reported anomalies in the low temperature region, Ni-Co-Mn-In, Cu-Al-Mn and Ti-Ni SMAs were selected and studied with regard to SE and/or SME behaviors, mainly at the cryogenic temperatures.

Chapter 2: Stress-Induced Martensitic Transformation at Low Temperatures in a $Ni_{45}Co_{5}Mn_{36}In_{14}$ Metamagnetic Shape Memory Alloy

In this chapter, stress-induced MT (SIT) behaviors in a $Ni_{45}Co_5Mn_{36}In_{14}$ alloy, which does not exhibit thermally-induced MT (TIT) down to the lowest temperature of 4.2 K, are presented in the temperature range of 4.2 - 200 K. At all the temperatures tested, almost perfect superelastic shape recovery was obtained and the critical stress for stress-induced transformation (σ_{Ms}) showed a concave temperature dependence in the forward transformation with decreasing temperature while that for reverse transformation (σ_{As}) monotonically decreased, resulting in a drastic increase of stress hysteresis (σ_{hys}) at low temperature. On the other hand, the equilibrium stress (σ_0), defined as the average of σ_{Ms} and σ_{As}, exhibited a tendency of temperature dependence decrement and converged to an almost constant value below ~150 K. The dissipation energy brought about by SIT, MFIT (magnetic-field induced MT) and TIT generally showed the same temperature dependence. This finding strikingly indicates that the driving forces to induce SIT, MFIT and TIT are equivalent and even that the total amount of excess energy for MT does not depend on the transformation route.

Chapter 3: Stress-Induced Martensitic Transformation at Low Temperatures in Cu-Al-Mn Shape Memory Alloys

In this chapter, three alloys, *i.e.*, Cu-17Al-15Mn and Cu-23Al-11,13Mn, which transform into 18R(6M) and 2H, respectively, were prepared. For Cu-17Al-15Mn, test specimens composed of different microstructures of single crystal, bamboo-like coarse grains (~2 mm in size) and fine grains (~200 μm in size) were examined to investigate the correlation between SE behavior and the density of the grain boundaries.

All the Cu-17Al-15Mn specimens showed SE down to the lowest temperature of 4.2 K and, especially in the single-crystalline sample, excellent superelastic properties, namely, small stress hysteresis and large superelastic strain of over 7%, were confirmed even at 4.2 K. On the other hand, the shape of the obtained stress-strain curve was considerably different for each sample and the flatness of the superelastic plateaus was lost in the fine-grained specimen because of the mixture of superelastic deformation and elastic deformation of the parent phase (and slip deformation at high temperature). In spite of such difference, the equilibrium stress exhibited a similar temperature dependence in all the samples tested, reflecting that the thermodynamical relationship of stability between the parent and martensite phases was, in principle, invariant to the change in the size of crystal grains.

With respect to the single-crystalline Cu-23Al-11,13Mn alloys, superelastic curves over a wide temperature range as well as a Cu-17Al-15Mn single crystal were obtained. In contrast to Cu-17Al-15Mn that maintained a significantly small σ_{hys} even at 4.2 K, σ_{hys} for the 2H martensitic transformation was considerably large and showed a linear increase with decreasing temperature.

Chapter 4: Stress-Induced Martensitic Transformation at Low Temperatures in a Ti-51.8Ni (at.%) Shape Memory Alloy

In this chapter, polycrystalline Ti-51.8Ni alloy, possibly being in a strain glass state at cryogenic temperatures, was prepared. It exhibited SE with almost complete shape recovery in the temperature range from 40 to 180 K. While σ_0 showed a temperature dependence similar to that of Ni-Co-Mn-In, a dramatic increase in σ_{hys} was found at temperatures where the alloy was possibly in a strain glass state, being totally different in its magnitude from those of NiCoMnIn and CuAlMn alloys. In addition, a significant increase in σ_{Ms} on cooling enabled the occurrence of "heating-induced forward transformation" under a stress of 750 MPa from the parent phase supercooled down to 4.2 K without stress.

Chapter 5: Discussion on the Temperature Dependence of Equilibrium Stress Based on the Thermodynamic Theory

Since σ_0 gives the approximate equilibrium conditions, the use of the Clausius-Clapeyron relationship for σ_0 allows the estimation of the entropy change (ΔS) during SIT. Figure 1 shows a series of temperature dependence of ΔS of the alloys prepared in this thesis: NiCoMnIn, CuAlMn and TiNi alloys. Of great interest is that all the ΔS curves totally converged to zero when temperature approaching 0 K. This can be understood as a reasonable phenomenon obeying the third law of thermodynamics. In contrast, there was a significant difference in increasing behaviors of ΔS among these alloys. The origin of such difference is described by the temperature dependences of ΔS constituting components: vibrational entropy, $S_{vib.}$; magnetic entropy, $S_{mag.}$; and electronic entropy, $S_{el.}$. That is, for NiCoMnIn, the large contribution of $S_{mag.}$ in the parent phase and the abnormal

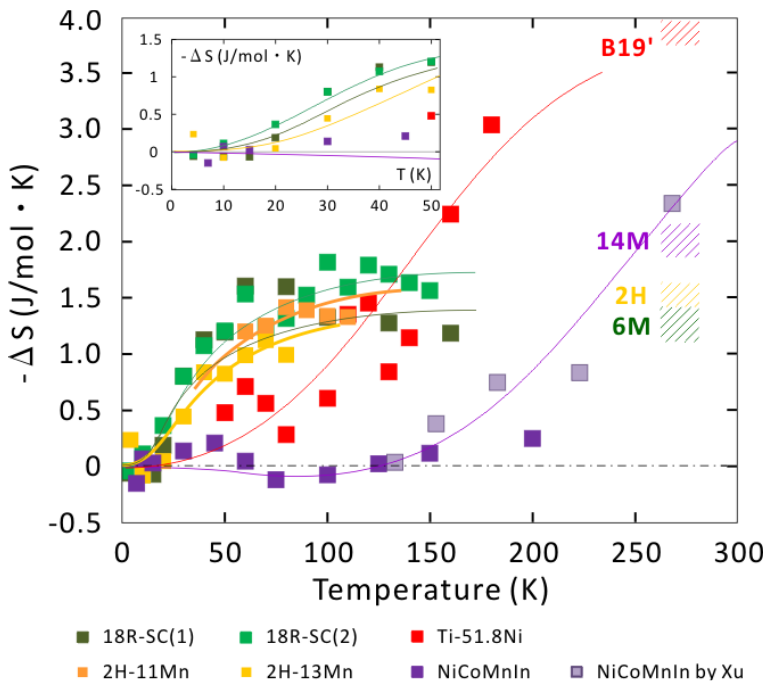

Fig. 1. Series of the temperature dependence of ΔS of the alloys prepared in this thesis.

relationship in Debye temperature of $\Theta_D^P > \Theta_D^M$ suppresses the increase in ΔS, allowing the occurrence of the TTA phenomenon. In contrast, for CuAlMn and TiNi alloys, the temperature dependences of ΔS are similar to the temperature dependences of $\Delta S_{vib.}$ with the estimated Debye temperatures of the parent and martensite phases.

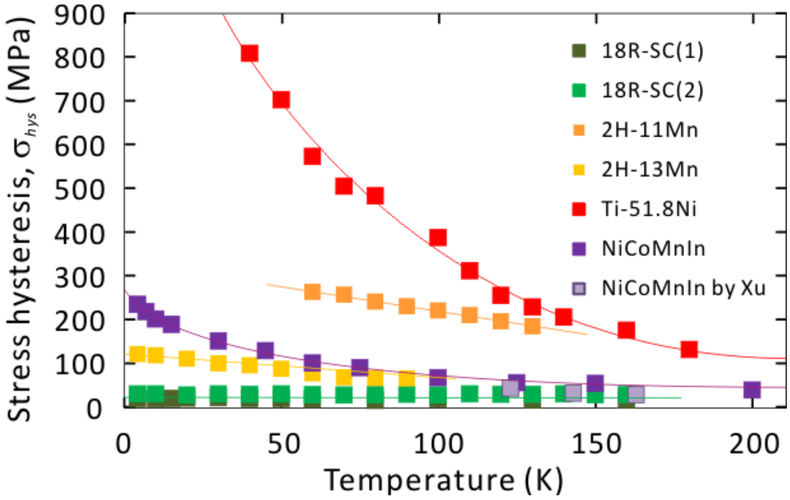

Fig. 2. Series of the temperature dependence of σ_{hys} of the alloys prepared in this thesis.

Chapter 6: Discussion on the Origin of the Increase in Stress Hysteresis at Low Temperature

Figure 2 shows a series of the temperature dependence of σ_{hys}. Larger σ_{hys} at lower temperatures introduces the occurrence of serration deformation, which brings about so-called cryogenic plasticity and yields larger latent heat during stress-induced transformation, being harmful for the surrounding low-temperature environment. In this chapter, a phenomenological understanding of the temperature dependence of σ_{hys} is offered and systematic investigations on the origin of the increase in σ_{hys} are made.

A phenomenological theory for the motion of habit planes was proposed by modifying Seeger's kinetic theory for CRSS of plastic deformation. The experimentally obtained σ_{hys} was successfully fitted using this proposed theory, and therefore, the origin of such increase was inferred to be due to the thermal activation process of the motion of habit planes. By the results of screening verifications, it was found that the magnitude and temperature dependency of the thermal activation component, $\sigma_{TA}(T)$, were strongly dependent on the combination of crystal structures before and after transformation rather than on the kinds of obstacles possibly yielding energy barrier. Considering that the growth of martensite variant involves the creation of defects (mainly, dislocations) and that the compatibility of the lattice greatly affects the window of (thermal) hysteresis (although the latter is verified only at temperatures where the athermal component is dominant), it was tentatively proposed that the $\sigma_{TA}(T)$ is uniquely determined by the amount and/or constituent of defects required to induce the martensitic transformation.

Chapter 7 Conclusions

In this chapter, the contents of chapters 1 through 6 are summarized.

論文審査結果の要旨

超弾性は、熱弾性型マルテンサイト(M)変態に起因する現象であり、その実用的有用性により基礎から応用に至るまで広く研究されてきた。しかしながら、特に77K以下の極低温領域における研究は従来ほとんど報告されていない。そこで本論文では、NiCoMnIn、CuAlMn、TiNi 合金の極低温領域における超弾性挙動を系統的に調査し、極低温域で動作可能な超弾性材料の探索を目的とする。

第１章は序論である。

第２章ではNiCoMnInメタ磁性形状記憶合金（SMA）の単結晶材において、4.2～200Kの温度範囲で良好な超弾性特性が得られることを確認した。同系は、M変態を温度・磁場・応力いずれの外場によっても誘起可能であることが知られているが、本研究結果からヒステリシスとして検出される変態に際しての散逸エネルギー量の温度依存性がどの変態モードでもほぼ一致することを明らかにした。

第３章ではCuAlMn系 SMA を対象合金とし低温域での超弾性特性を調査するとともに、M相の構造(6M及び 2H)および結晶粒径の超弾性特性への影響を系統的に調査した。いずれの合金、結晶粒径においても低温域での超弾性の発現を確認したが、とりわけ Cu-17Al-15Mn(at.%)単結晶材において、4.2K で非常に良好な超弾性特性（小さい応力ヒステリシス（SH）かつ約 7%に及ぶ大きな超弾性歪）を得ることができ、低温応用に適した材料であることを見出した。

第４章ではTiNi系 SMA（51.8at%Ni）において40-180Kの温度範囲で超弾性の発現を確認した。この組成域ではストレイングラスが報告されているが、そのような温度域においては変態に際してのSHが温度低下とともに異常に増大することを突き止めた。

第５章ではM変態開始および逆変態終了応力の平均を母相とM相が熱力学的に平衡する応力（平衡応力）と定義し、２～４章で取り上げた合金の平衡応力の温度依存性について熱力学的に考察した。平衡応力の温度依存性からクラウジウス・クラペイロンの式を通して見積もられる変態エントロピー変化(ΔS)は、どの合金においても極低温で 0 に収束するが、温度上昇に伴うΔSの振る舞いは、NiCoMnIn においては母相の磁気系エントロピー変化、CuAlMn、TiNi においては格子系エントロピー変化がその傾向を特徴づける主な支配的因子であることを明らかにした。

第６章では２～４章で取り上げた合金のSHの温度依存性について考察した。臨界せん断応力の温度依存性を現象論的に説明したSeegerの理論を拡張し、SH増大の起源が晶癖面移動の熱活性化過程にあると推察した。さらに熱活性化挙動の起源を解明するために、種々の欠陥を導入した条件で実験を行い、その結果を考察した。

第７章は結言である。

以上、本論文は、TiNiやCuAlMnといった実用SMAにおいてM変態が極低温域でも発現することを初めて確認し、低温応用への可能性を見出した。また、極低温域での母相/M相間の相平衡やSHの温度依存性を明確にするなど、学術的見地からの貢献も顕著である。なお、本研究成果の一部は投稿論文４報としてまとめられ、発表した国際会議においてポスター賞を受賞した。以上の様に本論文は博士論文として充分な学術的独創性と工学的有用性を有しており、金属フロンティア工学発展への寄与が少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。